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(54) Title: THICKENED, HIGHLY AQUEOUS, COST EFFECTIVE LIQUID DETERGENT COMPOSITIONS

(57) Abstract

Low cost, effective aqueous heavy duty liquid laundry detergent compositions are provided. Such compositions contain relatively low levels of an anionic/nonionic-based surfactant system along with a protease-containing enzyme component, a low-cost viscosity-enhancing agent and relatively large amounts of water. The anionic component of the surfactant system comprises a combination of alkyl sulfate and alkyl ether sulfate. The nonionic component of the surfactant system comprises fatty alcohol ethoxylates. Only minimal amounts of other detergent composition adjuvants are permitted in such compositions.

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THICKENED, HIGHLY AQUEOUS, COST EFFECTIVE LIQUID DETERGENT COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to heavy duty liquid (HDL) laundry detergent products which comprise a selected type of anionic/nonionic surfactant system, relatively large amounts of water as a liquid carrier and minimal amounts of additional functional and/or non-functional detergent composition adjuvants.

BACKGROUND OF THE INVENTION

Liquid detergent products are often considered to be more convenient to use than are dry powdered or particulate detergent products. Liquid detergents have therefore found substantial favor with consumers. Such liquid detergent products are readily measurable, speedily dissolved in the wash water, capable of being easily applied in concentrated solutions or dispersions to soiled areas on garments to be laundered and are non dusting. They also usually occupy less storage space than granular products. Additionally, liquid detergents may have incorporated in their formulations materials which could not withstand drying operations without deterioration, which operations are often employed in the manufacture of particulate or granular detergent products.

Liquid detergent products in terms of their most basic components will generally essentially comprise functional ingredients such as one or more surface active agents (surfactants) that promote and facilitate the removal of stains and soils from fabrics laundered in aqueous wash solutions formed from such liquid detergent products. Liquid detergent products will also generally contain a liquid carrier such as water which serves to dissolve or at least suspend the essential functional surfactant ingredients.

In addition to surfactants and a carrier liquid, heavy duty liquid detergent products can also contain a wide variety of additional functional ingredients which serve to boost the fabric cleaning effectiveness of the products into which they are

incorporated. Such additional functional ingredients can include, for example, various detergent builders, chelating agents, bleaching agents, bleach activators or catalysts, detergent enzymes, enzyme stabilizers, grease/oil solvents, dye transfer inhibition agents, pH controllers, brighteners and the like. While such additional composition components can enhance composition cleaning performance, such additional functional materials can also be relatively expensive, thereby driving up the cost of manufacture of such products and ultimately driving up the cost of such products to the consumer.

Liquid detergent products may also contain other types of additional ingredients which do not necessarily enhance the cleaning performance of such products but which may be useful for improving the physical stability or the aesthetics of such products. Such non-functional ingredients include a wide variety of materials such as hydrotropes, additional solvents, phase stabilizers, thickeners, suds suppressors, perfumes, dyes and the like. Again, while such non-functional ingredients can beneficially affect the stability or appearance of detergent products containing them, such non-functional ingredients also add cost to the product without necessarily serving to improve the fabric cleaning performance thereof.

Given the foregoing considerations, it is highly desirable when formulating liquid detergent products to arrive at a proper balance of such competing factors as composition cost, composition cleaning performance and composition stability or aesthetics. There remains a continuing need to identify heavy duty liquid laundry detergents with ingredients selected to provide suitably effective stain/soil removal from fabrics laundered therewith while at the same time minimizing the cost of such products. Accordingly, it is an object of the present invention to formulate heavy duty liquid laundry detergent compositions containing a selected cost effective surfactant system combined with relatively high concentrations of the most cost effective liquid detergent carrier - water.

It is a further object of the present invention to provide such liquid detergent compositions containing only minimal amounts of additional, relatively costly functional cleaning performance-enhancing ingredients.

It is the further object of the present invention to provide such liquid detergent compositions which also contain only minimal amounts of additional, relatively costly non-functional stability- or aesthetics-enhancing ingredients.

SUMMARY OF THE INVENTION

The present invention relates to heavy-duty liquid laundry detergent compositions which provide cost effective stain and soil removal performance when

used in fabric laundering operations. Such compositions consist essentially of: A) from about 4% to 16% by weight of a selected type of anionic surfactant component; B) from about 0.1% to 8% by weight of a selected type of nonionic surfactant component; C) from about 0.05% to 0.5% by weight of a selected type of enzyme component; D) from about 0.05% to 3% by weight of certain types of viscosity-enhancing agents; and E) from about 80% to 96% by weight of an aqueous, non-surface active liquid carrier.

The anionic surfactant component of such compositions is one which is substantially free of alkylbenzene sulfate anionic surfactant materials. Such a component does comprise alkyl sulfates having a C_8-C_{20} alkyl group and alkyl polyethoxylate sulfates having a C_8-C_{20} alkyl group and a polyethoxylate chain containing from about 1 to 20 ethylene oxide moieties. The weight ratio of alkyl sulfate to alkyl polyethoxylate sulfate in such an anionic surfactant component ranges from about 1:12 to 1:1.

The nonionic surfactant component is one which is substantially free of aromatic-based nonionic surfactants. Nonionic surfactants essentially comprise alcohol ethoxylates containing a C_8-C_{16} alkyl group and from about 1 to 16 ethylene oxide moieties.

The enzyme component of the compositions herein comprises one or more protease detergent enzymes. Such an enzyme component, however, should contain no more than about 0.01% by weight of other types of detergent enzymes.

The viscosity-enhancing agent component of the compositions herein includes halide and formate salts and polyacrylic copolymers having a molecular weight of from about 500,000 to 1,000,000. Combinations of these types of viscosity-enhancing agents may also be employed.

The aqueous, non-surface active liquid carrier is one which comprises primarily water. Such a carrier should comprise no more than about 5% by weight of liquids other than water.

DETAILED DESCRIPTION OF THE INVENTION

As noted, the liquid laundry detergent compositions herein essentially contain an anionic surfactant component, a nonionic surfactant component and a relatively large amount of an aqueous liquid carrier. Each of these essential components as well as optional ingredients for such compositions and methods of preparing and using such compositions are described in detail as follows: All concentrations and ratios discussed hereinafter are on a weight basis unless otherwise specified.

A) ANIONIC SURFACTANT COMPONENT

The detergent compositions herein comprise from about 4% to 16% by weight of an anionic surfactant component. Preferably, such compositions comprise from about 10% to 12% by weight of this anionic surfactant component.

The anionic surfactant component of the compositions herein itself comprises two essential types of anionic surfactant materials. These are alkyl sulfates and alkyl polyethoxylate sulfates.

i) Alkyl Sulfates

One essential ingredient of the anionic surfactant component comprises primary or secondary alkyl sulfate anionic surfactants. Such surfactants are those produced by the sulfation of higher C_8-C_{20} fatty alcohols.

Conventional primary alkyl sulfate surfactants have the general formula:

$$ROSO_3^-M^+$$

wherein R is typically a linear C_8-C_{20} hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. Preferably R is a C_{10}-C_{15} alkyl, and M is alkali metal. Most preferably R is C_{12}-C_{14} and M is sodium.

Conventional secondary alkyl sulfates may also be utilized in the essential anionic surfactant component of the compositions herein. Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure:

$$CH_2(CH_2)_n(CHOSO_3^-M^+)\,(CH_2)_mCH_3$$

wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 15, and M is a water-solubilizing cation.

Especially preferred types of secondary alkyl sulfates are the (2,3) alkyl sulfate surfactants which can be represented by structures of formulas A and B:

(A) $CH_2(CH_2)_x(CHOSO_3^-M^+)\,CH_3$ and

(B) $CH_3(CH_2)_y(CHOSO_3^-M^+)\,CH_2CH_3$

for the 2-sulfate and 3-sulfate, respectively. In formulas A and B, x and (y+1) are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably about 10 to about 16. M is a cation, such as an alkali metal, alkaline earth metal, or the like. Sodium is typical for use as M to prepare the water-soluble (2,3) alkyl sulfates, but potassium, and the like, can also be used.

ii) Alkyl Polyethoxylate Sulfates

The second essential ingredient of the anionic surfactant component comprises alkyl polyethoxylate sulfates. Such ethoxylated alkyl sulfates are those which correspond to the formula:

$$R'\text{-}O\text{-}(C_2H_4O)_n\text{-}SO_3M$$

wherein R' is a C_8-C_{20} alkyl group, n is from about 1 to 20, and M is a salt-forming cation. Preferably, R' is C_{10}-C_{18} alkyl, n is from about 1 to 15, and M is sodium, potassium, ammonium, alkylammonium, or alkanolammonium. Most preferably, R' is a C_{12}-C_{16}, n is from about 1 to 6 and M is sodium. These materials, also known as alkyl ether sulfates, can provide especially desirable fabric cleaning performance benefits when used in combination with the unethoxylated alkyl sulfates hereinbefore described.

The alkyl ether sulfates will generally be used in the form of mixtures comprising varying R' chain lengths and varying degrees of ethoxylation. Frequently such mixtures will inevitably also contain some unethoxylated alkyl sulfate materials, i.e., surfactants of the above ethoxylated alkyl sulfate formula wherein n=0.

iii) Alkyl Sulfate/Alkyl Polyethoxylate Sulfate Ratio

Within the anionic surfactant component, the weight ratio of alkyl sulfate to alkyl polyethoxylate sulfate should generally range from about 1:12 to 1:1. More preferably this ratio will range from about 1:4 to 1:1. In determining the ratio of alkyl sulfate to alkyl polyethoxylate sulfate materials, the amount of unethoxylated material in the alkyl polyethoxylate sulfate mixture is not taken into account. Rather, the weight ratios hereinbefore specified are determined on the basis of the ratio of these materials as separately added alkyl sulfate and alkyl polyethoxylate surfactant components.

iv) Optional Anionic Surfactants

In addition to the essentially utilized alkyl sulfate and ethoxylated alkyl sulfate surfactants, the anionic surfactant component of the compositions herein may also contain additional optional anionic surfactants so long as such additional optional anionic materials are compatible with other composition components and do not substantially adversely affect composition cost or performance, e.g., fabric cleaning performance or composition stability. Optional anionic surfactants which may be employed include in general the carboxylate-type anionics. Carboxylate-type anionics include fatty acid, e.g., C_{10}-C_{18}, soaps, the C_{10}-C_{18} alkyl alkoxy

carboxylates (especially the EO 1 to 5 ethoxycarboxylates) and the C_{10}-C_{18} sarcosinates, especially oleoyl sarcosinate.

One common type of anionic surfactant which should not be utilized in the anionic surfactant component of the compositions herein comprises the sulfonated anionics which are alkyl benzene sulfonates. Alkyl benzene sulfonates are desirably avoided in formulating the liquid detergent products herein for processing and/or other reasons. Accordingly, the anionic surfactant component of the detergent compositions herein should be substantially free of such alkyl benzene sulfonate anionic surfactant materials.

B) NONIONIC SURFACTANT COMPONENT

The detergent compositions herein also essentially comprise from about 0.1% to 8% by weight of a nonionic surfactant component. Preferably, such compositions will comprise from about 1% to 3% by weight of this nonionic surfactant component.

The nonionic surfactant component essentially comprises one specific type of nonionic surfactant material - fatty alcohol ethoxylates.

i) Fatty Alcohol Ethoxylates

Fatty alcohol ethoxylate nonionic surfactant materials useful herein are those which correspond to the general formula:

$$R^1(C_2H_4O)_nOH$$

wherein R^1 is a C_8-C_{16} alkyl group and n ranges from about 1 to 16. Preferably R^1 is an alkyl group, which may be primary or secondary, that contains from about 9 to 15 carbon atoms, more preferably from about 10 to 14 carbon atoms. Preferably the ethoxylated fatty alcohols will contain from about 2 to 12 ethylene oxide moieties per molecule, more preferably from about 3 to 10 ethylene oxide moieties per molecule.

The ethoxylated fatty alcohol nonionic surfactant will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from about 3 to 17. More preferably, the HLB of this material will range from about 6 to 15, most preferably from about 10 to 15.

Examples of fatty alcohol ethoxylates useful as the essential liquid nonionic surfactant in the compositions herein will include those which are made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials have been commercially marketed under the tradenames Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an ethoxylated primary

C_{12}-C_{13} alcohol having about 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C_9-C_{11} primary alcohol having about 10 moles of ethylene oxide. Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol tradename. Dobanol 91-5 is an ethoxylated C_9-C_{11} fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C_{12}-C_{15} fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohol nonionic surfactants include Tergitol 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates that have been commercially marketed by Union Carbide Corporation. The former is a mixed ethoxylation product of C_{11} to C_{15} linear secondary alkanol with 7 moles of ethylene oxide and the latter is a similar product but with 9 moles of ethylene oxide being reacted.

Other types of alcohol ethoxylate nonionics useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products have also been commercially marketed by Shell Chemical Company.

ii) Optional Nonionics

So long as the nonionic surfactant component of the compositions herein contains the foregoing type of fatty alcohol ethoxylate nonionic surfactant, the nonionic surfactant component may also optionally include additional compatible, non-interfering nonionics if cost considerations permit. These can include, for example, C_{10}-C_{18} alkyl polyglucosides when high foaming compositions are desired; polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamides. (The N-propyl through N-hexyl C_{12}-C_{16} glucamides can be used for low sudsing performance.); ethylene oxide-propylene oxide block polymers of the Pluronic type; and the like. If utilized at all, such optional nonionic surfactant materials should comprise no more than about 0.2% by weight of the detergent compositions herein.

One common type of nonionic surfactant which should not be utilized in the nonionic surfactant component of the compositions herein comprises the aromatic-based nonionics such as the alkylphenols. Aromatic-based nonionic materials are desirably avoided in formulating the liquid detergent products herein for possible environmental and/or other reasons. Accordingly, the nonionic surfactant

component of the detergent compositions herein should be substantially free of such aromatic-based nonionic surfactants.

C) PROTEASE ENZYME COMPONENT

The third essential component of the compositions herein comprises detergent enzyme material that contains one or more protease enzymes. Such an enzyme component will generally comprise from about 0.05% to 0.5% by weight of the compositions herein, more preferably from about 0.2% to 0.4% by weight of the compositions herein. Within this enzyme component, one or more protease enzyme materials will generally be present in an amount sufficient to provide from about 0.005 to 0.1 Anson units (AU) of protease activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. *subtilis* and B. *licheniforms*. Another suitable protease is obtained from a strain of Bacilus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al., published January 9, 1985). All of these patent publications are incorporated herein by reference.

Other types of detergent enzymes have also been widely employed in detergent compositions. Such enzymes as lipases, amylases, cellulases, and peroxidases are well known. It is possible to add one or more of these non-protease type of enzymes to the detergent compositions herein the improve the effectiveness of the composition in removing certain types of soils/stains. However, for purposes of the present invention, it has been determined that the incorporation of these non-protease enzyme types into the compositions herein is not especially cost effective. Accordingly, the enzyme component of the detergent compositions of this invention will generally contain no more than about 0.01% by weight of the composition of non-protease enzyme materials.

D) VISCOSITY-ENHANCING AGENT COMPONENT

The fourth essential component of the liquid detergent compositions herein comprises one or more relatively low cost viscosity-enhancing agents. Such viscosity-enhancing agents, i.e., thickeners, will generally comprise from about 0.05% to 3% by weight of the compositions herein, more preferably, from about 0.1% to 2% by weight of the compositions herein.

The relatively low cost viscosity-enhancing agents which are especially suitable for use in the highly aqueous liquid detergents of this invention can include halide and formate salts as well as polyacrylic co-polymers. Combinations or mixtures of these types of viscosity-enhancing agents can also be employed.

Suitable halide and formate salts which may be utilized include the alkali metal, alkaline earth metal and magnesium salts of halides and formates. Examples of such materials include sodium chloride, potassium chloride, calcium chloride, magnesium chloride, sodium bromide, sodium formate, calcium formate, and magnesium formate. Sodium chloride, sodium formate, and calcium formate are the most preferred.

The polyacrylic co-polymers which may be utilized as viscosity-enhancing agents are those having a molecular weight of from about 500,000 to 1,000,000, more preferably from about 750,000 to 1,000,000. Suitable co-monomers for use in preparing these materials include methacrylic acid and ethylene oxide. These polyacrylic thickeners may or may not be cross-linked. Examples of suitable polyacrylic copolymer thickening agents include those marketed under the tradenames Acusol 820 and Acusol 880 by Rohm and Haas Company.

E) AQUEOUS LIQUID CARRIER

The fifth essential component of the liquid detergent compositions herein comprises an aqueous, non-surface active liquid carrier. Since the objective of the present invention is to utilize as little as possible of the functional detergent composition components, the amount of the aqueous, non-surface active liquid carrier employed in the compositions herein will be relatively large. Generally, the non-aqueous, non-surface active liquid carrier component will comprise from about 80% to 96% by weight of the compositions herein. More preferably this liquid carrier component will comprise from about 82% to 90% by weight of the compositions herein.

The most cost effective type of aqueous, non-surface active liquid carrier is, of course, water itself. Accordingly, the aqueous, non-surface active liquid carrier component will generally be mostly, if not completely, comprised of water. While

other types of water-miscible liquids, such alkanols, diols, other polyols, ethers, amines, and the like, have been conventionally been added to liquid detergent compositions as co-solvents or stabilizers, for purposes of the present invention, the utilization of such water-miscible liquids should be minimized, if not eliminated. Thus, the aqueous, non-surface active liquid carrier component of the compositions herein will generally contain no more than about 5% by weight of the composition of liquids other than water. Preferably, the liquid carrier will contain no more than about 2% by weight of the composition of liquids other than water.

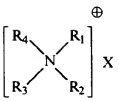
F) OPTIONAL DETERGENT COMPOSITION INGREDIENTS

The detergent compositions of the present invention can also include any number of additional optional ingredients. These include conventional detergent composition components such as optional surfactants, builders, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzyme stabilizers such as propylene glycol, boric acid and/or borax, hydrotropes, dye transfer inhibiting agents, brighteners, and perfumes. In keeping with the purpose of the present invention, such optional ingredients, if used, must be incorporated at relatively low levels, and indeed at levels generally below those at which they are conventionally employed if cost effective compositions are to be realized. Accordingly, if used, such optional ingredients will generally comprise no more than about 3%, i.e., from about 0.001% to 2%, by weight of the compositions herein. A few of the optional ingredients which can be used are described in greater detail as follows:

i) Optional Surfactants

In addition to the optional anionic and nonionic surfactants hereinbefore described, the detergent compositions herein may contain other types of compatible surfactant materials. These include surfactants of the cationic and amphoteric types. Examples of such materials include quaternary ammonium cationics, C_{10}-C_{18} amine oxides and the C_{12}-C_{18} betaines and sulfobetaines. The most preferred of these optional surfactants comprises the quaternary ammonium cationics.

Quaternary ammonium cationic surfactants include of those of the formula:



wherein R_1 and R_2 are individually selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5; X is an anion; and (1) R_3 and R_4 are each a C_8-C_{14} alkyl or (2) R_4 is a C_8-C_{22} alkyl and R_3 is selected from the group consisting of C_1-C_{10} alkyl, C_1-C_{10} hydroxy alkyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5.

Preferred of the above are the mono-long chain alkyl quaternary ammonium surfactants wherein the above formula R_1, R_2, and R3 are each methyl. and R_4 is a C_8-C_{18} alkyl. The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate C_8-C_{16} alkyl trimethyl ammonium salts, and C_8-C_{16} alkyl di(hydroxyethyl)-methyl ammonium salts. Of the above, lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride and coconut trimethylammonium chloride and methylsulfate are particularly preferred. ADOGEN 412™, a lauryl trimethyl ammonium chloride commercially available from Witco, is a preferred quaternary ammonium cationic surfactant.

Quaternary ammonium cationic surfactants of the foregoing type are known to be useful in detergent compositions as fabric softening agents. However, such materials, if used in the compositions of the present invention, are generally used at concentrations below those useful for such materials to provide fabric softening effects. When employed at concentrations of from about 0.1% to 1% by weight, more preferably from about 0.5% to 0.8% by weight of the composition, such quaternary ammonium cationics will provide a grease/oil soil removal performance benefit without undesirably driving up the cost of the compositions herein. When employed in these relatively low concentrations, such quaternary ammonium cationics can also act as thickeners which increase the viscosity of the liquid detergent compositions herein.

ii) Optional Organic Detergent Builders

The detergent compositions herein may also optionally contain low levels of an organic detergent builder material which serves to counteract the effects of calcium, or other ion, water hardness encountered during laundering/bleaching use of the compositions herein. Examples of such materials include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates,

polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids C_{10}-C_{22} fatty acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those which have been sold by Monsanto under the Dequest tradename and alkanehydroxy phosphonates. Citrate salts and C_{12}-C_{18} fatty acid soaps are highly preferred.

Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the Sokalan trademark.

If utilized, optional organic builder materials will generally comprise from about 0.1% to 1%, more preferably from about 0.1% to 0.4%, by weight of the compositions herein. Even at such concentrations which are generally lower than those conventionally utilized, organic builders can serve to enhance the cost effective fabric laundering performance of the liquid detergent compositions herein.

iii) Enzyme Stabilizers

The detergent compositions herein may also optionally contain low levels of materials which serve to maintain the stability of the enzyme materials of the enzyme component. Such enzyme stabilizers can include, for example, polyols such as propylene glycol. boric acid and borax. Combinations of these enzyme stabilizers may also be employed. If utilized, enzyme stabilizers can comprise from about 0.1% to 1% by weight of the compositions herein.

iv) Phase Stabilizers/Co-solvents

The detergent compositions herein may also optionally contain low levels of materials which serve as phase stabilizers and/or co-solvents for the liquid compositions herein. Materials of this type include C_1-C_3 lower alkanols such as methanol, ethanol and/or propanol. Lower C_1-C_3 alkanolamines such as mono-, di- and triethanolamines can also be used, by themselves or in combination with the lower alkanols. If utilized, phase stabilizers/co-solvents can comprise from about 0.1% to 0.5%by weight of the compositions herein.

v) pH Control Agents

The detergent compositions herein may also optionally contain low levels of materials which serve to adjust or maintain the pH of the aqueous detergent

compositions herein at optimum levels. The pH of the compositions of this invention should range from about 9.2 to 10. Materials such as NaOH can be added to alter composition pH, if necessary.

G) COMPOSITION FORM, PREPARATION AND USE

The liquid detergent compositions herein are in the form of an aqueous solution or uniform dispersion or suspension of anionic surfactant, enzymes and certain optional other ingredients, all of which are normally in solid form, which have been combined with the normally liquid components of the composition such as the liquid alcohol ethoxylate nonionic, the aqueous liquid carrier, and any other normally liquid optional ingredients. Such a solution, dispersion or suspension will be acceptably phase stable and will typically have a viscosity which ranges from about 5 to 300cps, more preferably from about 50 to 250cps. For purposes of this invention, viscosity is measured with a Brookfield LVTDV-11 apparatus using an RV #2 spindle at 12 rpm.

The aqueous liquid detergent compositions herein can be prepared by combining the essential and optional components thereof in any convenient order and by mixing, e.g., agitating, the resulting component combination to form the phase stable compositions herein. In a preferred process for preparing such compositions, essential and certain preferred optional components will be combined in a particular order. In such a preferred preparation process, a liquid matrix is formed containing at least a major proportion, and preferably substantially all, of the liquid components, e.g., the essential alcohol ethoxylate nonionic surfactant, the aqueous, non-surface active liquid carrier and other optional liquid components with the liquid components being thoroughly admixed by imparting shear agitation to this liquid combination. For example, rapid stirring with a mechanical stirrer may usefully be employed.

While shear agitation is maintained, substantially all of the essential anionic surfactants, viscosity-enhancing agents, optional cationic surfactants, and optional builders can be added in the form of particles ranging in size from about 0.2 to 1,000 microns. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a solution or a uniform dispersion of insoluble solid phase particulates within the liquid phase.

After some or all of the solid-form materials have been added to this agitated mixture, the particles of the enzyme material, e.g., enzyme prills, are incorporated. Thus the enzyme component is preferably added to the aqueous liquid matrix last.

As a variation of the composition preparation procedure hereinbefore described, one or more of the solid components may be added to the agitated mixture as a solution or slurry of particles premixed with a minor portion of one or more of

the liquid components. In another variation of the preparation procedure, the viscosity-enhancing agent may be added by combining it with the anionic surfactant during preparation of the anionic surfactant component. In this way, the viscosity-enhancing agent (such as sodium formate) can be introduced into the compositions herein via the anionic surfactant when the anionic is combined with the rest of the detergent composition components.

After addition of all of the composition components. agitation of the mixture is continued for a period of time sufficient to form compositions having the requisite viscosity and phase stability characteristics. Frequently this will involve agitation for a period of from about 30 to 60 minutes.

The compositions of this invention, prepared as hereinbefore described, can be used to form aqueous washing solutions for use in the laundering of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous washing solution. More preferably, from about 1,000 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing solution.

EXAMPLES

The following examples illustrate the compositions of the present invention but are not necessarily meant to limit or otherwise define the scope of the invention herein.

EXAMPLE I

A composition of the present invention is prepared by mixing together the ingredients listed in Table I in the proportions shown.

Table I

Liquid Detergent Composition

Component	Wt % Active
C_{12-14} Alkyl polyethoxylate (3.0) sulfonic acid (27%)	6.0
C_{12-14} Alkyl sulfate	6.0
C_{12-13} Alcohol Ethoxylate* (EO=9)	2.0
Citric acid (50%)	0.15
Protease Enzyme (34 g/l)	0.45
Propylene Glycol	0.28
Monoethanolamine	0.16
Borax (38%)	0.6
NaOH (50%)	1.88
Sodium Formate (30%)	0.85
Silicone Suds Suppresser	0.035
Dye	0.0048
Perfume	0.24
Brightener	0.05
Water	Balance
	100%

*** Neodol 23-9**

The Table I liquid detergent composition provides very effective fabric cleaning performance when used to form aqueous wash solutions for conventional fabric laundering operations. Such performance is provided and the composition is stable, even thougn the composition is relatively low cost due to the incorporation of only very small amounts of the surfactants and other composition adjuvants. By virtue of the use of sodium formate in the Table I composition, this liquid detergent product is also thick enough to be utilized as a pretreat product when it is applied full strength directly onto fabric stains prior to laundering of the stained fabrics. Compositions of substantially similar viscosity character can be realized if, in the Table I composition, the sodium formate is replaced with an equivalent amount of the polyacrylic co-polymer materials Acusol 820 or Acusol 880.

EXAMPLE II

Another composition of the present invention is prepared by mixing together the ingredients listed in Table II in the proportions shown.

Table II

Liquid Detergent Composition

Component	Wt. % Active
C_{12-14} Alkyl polyethoxylate (3.0) sulfonic acid (27%)	5.0
C_{12-14} Alkyl sulfate	5.0
C_{12-13} Alcohol Ethoxylate* (EO=9)	2.0
Lauryl trimethyl ammonium chloride**(37%)	0.7
Citric acid (50%)	0.15
Protease Enzyme (34 g/l)	0.45
Propylene Glycol	0.28
Monoethanolamine	0.16
Borax (38%)	0.6
NaOH (50%)	1.88
Na Cl	1.0
Silicone Suds Suppresser	0.035
Dye	0.0048
Perfume	0.24
Brightener	0.05
Water	Balance
	100%

*** Neodol 23-9**

****Adogen 412**

The Table II liquid detergent composition provides very effective fabric cleaning performance when used to form aqueous wash solutions for conventional fabric laundering operations. The addition of the quaternary ammonium cationic surfactant serves to enhance the greasy/oily stain removal performance of such a composition and also serves to increase its viscosity.

What is Claimed is:

1. A heavy duty liquid laundry detergent composition which provides cost effective stain and soil removal performance when used in fabric laundering operations, which composition is characterized in that it comprises:

(A) from 4% to 16%, preferably 10% to 12%, by weight of the composition of an anionic surfactant component which is substantially free of alkyl benzene sulfonate anionic surfactant materials and which comprises

i) alkyl sulfates wherein the alkyl group contains from 8 to 20, preferably 10 to 15, carbon atoms; and

ii) alkyl polyethoxylate sulfates wherein the alkyl group contains from 8 to 20, preferably 10 to 18, carbon atoms and polyethoxylate chain contains from 1 to 20, preferably 1 to 15, ethylene oxide moieties;

in an alkyl sulfate to alkyl polyethoxylate sulfate weight ratio of from 1:12 to 1:1, preferably 1:4 to 1:1;

(B) from 0.1% to 8%, preferably 1% to 3%, by weight of the composition of a nonionic surfactant component which is substantially free of aromatic-based nonionic surfactants and which comprises fatty alcohol ethoxylates of the formula $R^1 (OC_2H_4)_nOH$ wherein R^1 is a C_8-C_{16}, preferably C_9-C_{15}, alkyl group and n is from 1 to 16, preferably 2 to 12; and

(C) from 0.05% to 0.5%, preferably 0.2% to 0.4%, by weight of the composition of an enzyme component which comprises one or more protease enzymes but contains no more than 0.01% by weight of said composition of other types of detergent enzymes; and

(D) from 0.05% to 3%, preferably 0.1% to 2%, by weight of a viscosity-enhancing agent selected from halide and formate salts; polyacrylic co-polymers having a molecular weight of from 500,000 to 1,000,000 and combinations of said salts and co-polymers; and

(E) from 80% to 96%, preferably 82% to 90%, by weight of the composition of an aqueous, non-surface active liquid carrier which comprises no more than 5% by weight of the composition of liquids other than water.

2. A composition according to Claim 1 wherein the fatty alcohol ethoxylate has an HLB of from 3 to 17 and wherein the composition contains from 0.1% to 1% by weight of an organic detergent builder.

3. A composition according to Claim 1 or Claim 2 wherein the protease is derived from Bacillus bacteria.

4. A composition according to any of Claims 1 to 3 which additionally contains from 0.1% to 1% by weight of the composition of one or more enzyme stabilizing agents selected from propylene glycol, boric acid and borax.

5. A composition according to any of Claims 1 to 4 which additionally contains from 0.1% to 0.5% by weight of the composition of a phase stabilizing/co-solvent agent selected from C_1-C_3 lower alkanols, mono-, di- and tri-lower C_1-C_3 alkanolamines and combinations thereof.

6. A composition according to any of Claims 1 to 5 which additionally contains from 0.1% to 1% by weight of the composition of a quaternary ammonium cationic surfactant.

7. A composition according to Claim 6 wherein the quaternary ammonium cationic surfactant is a C_8-C_{18} alkyl trimethyl ammonium salt.

8. A heavy duty liquid laundry detergent composition which provides cost effective stain and soil removal performance when used in fabric laundering operations, which composition is characterized in that it comprises:

(A) from 10% to 12% by weight of the composition of an anionic surfactant component which is substantially free of alkyl benzene sulfonate anionic surfactant materials and which comprises

i) sodium C_{12}-C_{14} alkyl sulfates; and

ii) sodium C_{12}-C_{16} alkyl ether sulfates containing from 1 to 6 moles of ethylene oxide;

in an alkyl sulfate to alkyl ether sulfate weight ratio of from 1:4 to 1:1;

(B) from 1% to 3% by weight of the composition of a nonionic surfactant component which is substantially free of aromatic-based nonionic surfactants and which comprises C_{10}-C_{14} fatty alcohol ethoxylates containing from 3 to 10 moles of ethylene oxide;

(C) from 0.1% to 0.4% by weight of the composition of a sodium citrate detergent builder;

(D) from 0.2% to 0.4% by weight of the composition of an enzyme component which comprises one or more protease enzymes derived

from Bacillus bacteria but contains no more than 0.01% by weight of said composition of other types of detergent enzymes;

(E) from 0.1% to 2% by weight of a viscosity-enhancing agent component selected from alkali metal and alkaline earth metal chlorides and formates; polyacrylic copolymers having a molecular weight of from 750,000 to 1,000,000 and combinations of viscosity-enhancing agents; and

(F) from 0.1% to 1% by weight of the composition of one or more enzyme stabilizers selected from propylene glycol, boric acid, borax and combinations thereof;

(G) from 82% to 90% by weight of the composition of an aqueous, non-surface active liquid carrier which comprises no more than 2% by weight of the composition of liquids other than water; and

(H) from 0.1% to 0.5% by weight of the composition of phase stabilizers/viscosity control agents selected from methanol, ethanol, monoethanolamine, diethanolamine, triethanolamine and combinations thereof.

9. A composition according to Claim 8 which additionally contains a pH control agent, preferably NaOH, suitable for maintaining compositon pH between 9.2 and 10.

10. A composition according to Claim 8 or Claim 9 which additionally contains from 0.001% to 2% by weight of the composition of one or more additional detergent composition adjuvants selected from non-protease enzymes, brighteners, dyes, suds control agents and perfumes.

11. A heavy duty liquid laundry detergent composition which provides cost effective stain and soil removal performance when used in fabric laundering operations, which composition is characterized in that it comprises:

(A) from 10% to 12% by weight of the composition of an anionic surfactant component which is substantially free of alkyl benzene sulfonate anionic surfactant materials and which comprises

i) alkyl sulfates wherein the alkyl group contains from 10 to 14, preferably 12 to 14, carbon atoms; and

ii) alkyl polyethoxylate sulfates wherein the alkyl group contains from 10 to 18, preferably 12 to 16, carbon atoms and the

polyethoxylate chain contains from 1 to 15, preferably 1 to 6, ethylene oxide moieties;

in an alkyl sulfate to alkyl polyethoxylate sulfate weight ratio of from 1:4 to 1:1;

(B) from 1% to 3% by weight of the composition of a nonionic surfactant component which is substantially free of aromatic-based nonionic surfactants and which comprises alcohol ethoxylates of the formula $R^1(OC_2H_4)_nOH$ wherein R^1 is a C_9-C_{15} alkyl group and n is from 2 to 12; and

(C) from 0.5% to 0.8% by weight of the composition of a cationic surfactant component selected from C_{10}-C_{22} alkyltrimethyl ammonium salts;

(D) from 0.12% to 0.4% by weight of the composition of a carboxylate detergent builder selected from C_{10}-C_{22} fatty acids and salts and citric acid and its salts.

(E) from 0.2% to 0.4% by weight of the composition of an enzyme component which comprises one or more protease enzymes but contains no more than 0.01% by weight of said composition of other types of detergent enzymes;

(F) from 0.1% to 2% by weight of a sodium chloride, sodium formate or calcium formate viscosity-enhancing agent and

(G) from 82% to 90% by weight of the composition of an aqueous, non-surface active liquid carrier which comprises no more than 2% by weight of the composition of liquids other than water; and

(H) from about 0.001% to 2% by weight of the composition of one or more detergent composition adjuvants selected from additional solvents, non-protease enzymes, enzyme stabilizers, hydrotropes, brighteners, dyes, suds control agents and perfumes.

12. A composition according to Claim 11 which contains from 0.1% to 1% by weight of the composition of one or more enzyme stabilizing agents selected from propylene glycol, boric acid, and borax.

13. A composition according to Claim 11 or Claim 12 which additionally contains from 0.1% to 0.5% by weight of the composition of a phase stabilizing/co-solvent agent selected from C_1-C_3 lower alkanols, mono-, di- and tri-lower C_1-C_3 alkanolamines and combinations thereof.

14. A composition according to any of Claims 11 to 13 wherein the alkyl sulfate is sodium lauryl sulfate.

15. A composition according to any of Claims 11 to 14 wherein the detergent builder is sodium citrate and the viscosity-enhancing agent is sodium formate.

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INTERNATIONAL SEARCH REPORT

Int. onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386 C11D1/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 030 378 (VENEGAS MANUEL G) 9 July 1991 see claim 1; examples I-C	1
P,A	WO,A,95 30734 (PROCTER & GAMBLE) 16 November 1995 see page 3, line 17 - line 19; example I	1-15
A	EP,A,0 167 382 (PROCTER & GAMBLE) 8 January 1986 see page 11, line 7 - line 9; claim 1; example IV	1,2
A,P A	US,A,5 419 853 (KEMEN KENNETH M) 30 May 1995 see examples & JP,A,06 057 299 (PROCTER & GAMBLE) 1 March 1994	1-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. ...nal Application No
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5030378	09-07-91	NONE		
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